

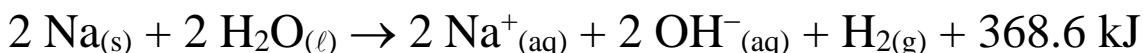
Chapter-19

Lesson-1

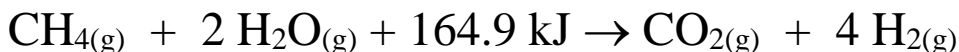
I – Spontaneous Processes

A) Reaction Spontaneity and Enthalpy Change:

- **Most (but not all) exothermic reactions are spontaneous and most (but not all) endothermic reactions are nonspontaneous.**



When sodium is added to water a violent exothermic reaction occurs (spontaneously) almost immediately.



Hydrogen gas is produced industrially from methane gas and steam, but the reaction is not spontaneous at 373 K.

- **The simple rule above often fails for many phase changes.**



- **THUS, ENTHALPY ALONE DOES NOT DETERMINE THE SPONTANEITY OF A PARTICULAR REACTION!**
- **Recall:** $\Delta H_{\text{Reaction}} = \Sigma \Delta H_{\text{f products}} - \Sigma \Delta H_{\text{f reactants}}$
- ΔH_{f} of a compound is the enthalpy change when one mole of the compound is formed from its free elements in their stable forms.
- ΔH_{f} of an element in its most stable form is zero.

Q1: Using heats of formation, calculate the heat of reaction of

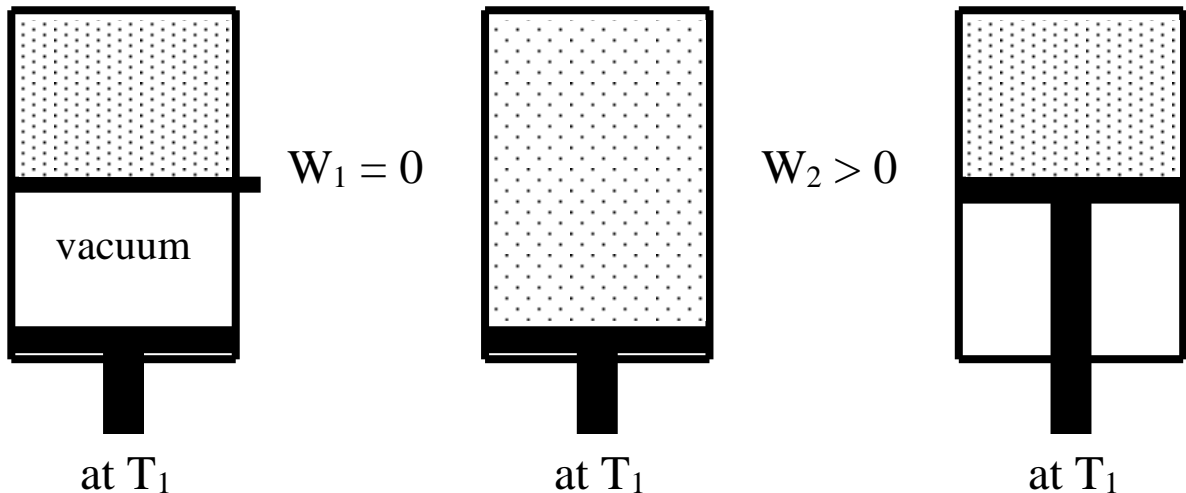


A1: $\Delta H = [2(-240.1) + 2(-230.0) + (0)] - [2(0) + 2(-285.8)]$

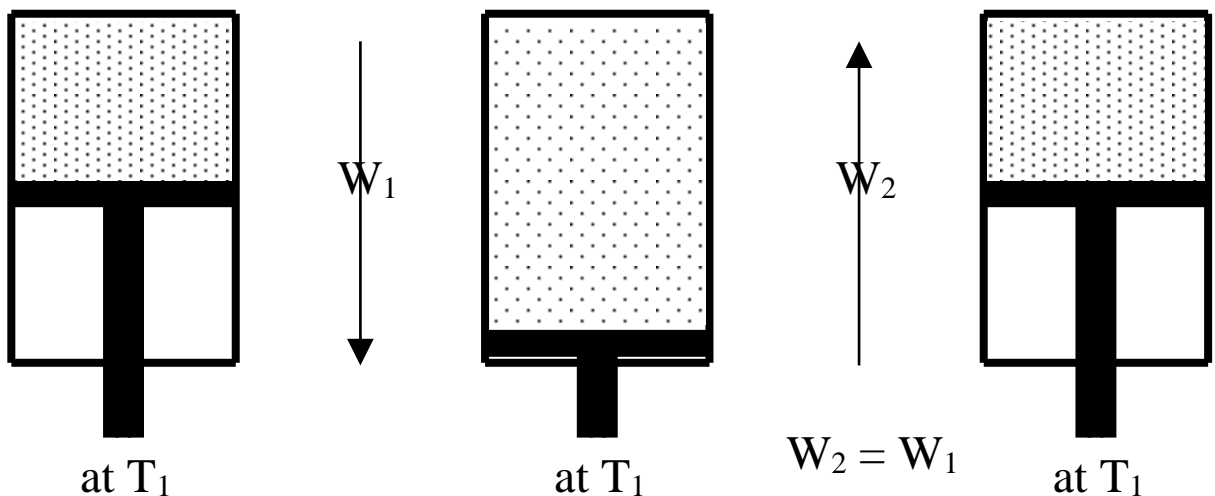
$$\Delta H = [-940.2] - [-571.6] = \boxed{-368.6 \text{ kJ/mol}} \text{ (exothermic)}$$

B) Reversible and Irreversible Processes:

- An **irreversible process** is one in which the conditions of the system and surroundings cannot be restored to their original state by simply reversing the process. To restore a system to its original state after an irreversible process has taken place, the conditions of the surroundings must change. [$W_{\text{before}} \neq W_{\text{after}}$]



- Work is done by the surroundings to reverse the process!
- A **reversible process** is one in which the conditions of the system and surroundings can be restored to their original state by simply reversing the process.



- A **reversible process** is one that reverses direction whenever an infinitesimal change is made in some property of the system.
- Since the reverse of a spontaneous reaction is a nonspontaneous reaction and since a nonspontaneous reaction can only occur if the surroundings do work on it (the reaction system), then **all spontaneous reactions are irreversible!**

II - Entropy & the Second Law of Thermodynamics

- Another factor that must be considered in order to determine whether a reaction will be spontaneous at a given temperature and pressure is called entropy (S).
- ①Entropy (S) is a measure of the extent of the randomness or disorder in a system. ②Entropy is a measure of the number of different ways energy can be distributed (or stored) in a system.
- The entropy of a system is a state function. $\Delta S = S_{\text{final}} - S_{\text{initial}}$
- Entropy *increases* as a substance goes from...
solid \rightarrow liquid \rightarrow gas.
- Entropy usually *increases* as **solid \rightarrow aqueous**.
- Entropy usually *decreases* when **gas \rightarrow aqueous**.
- Entropy *increases* when particle concentration decreases (+ ΔV).
- Entropy *usually increases* for a reaction that produces more moles of gas.
- **Reactions with an increase in entropy tend to be spontaneous.**

A) Entropy Changes for Isothermal Processes:

- An isothermal process is one that occurs at a constant temperature.
- The change in entropy for all isothermal processes is equal to the ratio of the heat that would be transferred if the processes were reversible to the temperature at which the process occurs.

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

- Since ΔS is a state function, the equation above can be used to determine in entropy change for any isothermal process whether it is reversible or not!
- All phase changes are isothermal processes.

Q2: What is the ΔS of an 18.0 g ice cube when it melts ($T = T_f$)?

A2: $\Delta S = q_{\text{rev}}/T = \Delta H_{\text{fusion}}/T$

$$\Delta S = [(+334 \text{ J/g}) \times (18.0 \text{ g})] \div [273 \text{ K}] = \boxed{+22.0 \text{ J/K}} \leftarrow \text{notice units!}$$

- The change in entropy for an **ideal gas** at constant temperature is:

$$\Delta S = nR \cdot \ln(V_2/V_1) \text{ or } \Delta S = nR \cdot \ln(P_1/P_2) \text{ where } R = 8.314 \text{ J/mol}\cdot\text{K}$$

Q3: What is the ΔS of 1.00 mole of an ideal gas at 298 K as it expands from 24.5 L to 30.0 L?

A3: $\Delta S = nR \cdot \ln(V_2/V_1)$

$$\Delta S = [(1.00)(8.314)] \cdot [\ln(30.0/24.5)] = +1.68 \text{ J/K}$$

Notice that the ΔS is positive. The entropy of a gas increases when it expands and decreases when it is compressed.

B) The Second Law of Thermodynamics

- For a spontaneous reaction, the enthalpy change (ΔH) may be positive (an endothermic reaction) or negative (an exothermic reaction).
- However, the total entropy change (ΔS_{total}) for all spontaneous reactions (irreversible processes) is always positive! This is known as the **second law of thermodynamics**.
- Total entropy change (ΔS_{total}) must take into account the entropy change of both the system and the surroundings.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \quad \Delta S_{\text{total}} > 0$$

- For a reversible process, the $\Delta S_{\text{total}} = 0$!

Q4: What is the ΔS_{total} for the melting of an 18.0g ice cube when it is held in one's fist?

A4: $\Delta S_{\text{ice}} = q_{\text{rev}}/T = \Delta H_{\text{fusion}}/T$

$$\Delta S_{\text{ice}} = [(+334 \text{ J/g}) \times (18.0 \text{ g})] \div [273 \text{ K}] = +22.0 \text{ J/K} \leftarrow \text{for ice cube (system)}$$

$$\Delta S_{\text{fist}} = -q_{\text{rev}}/T_{\text{body}} = -\Delta H_{\text{fusion}}/T_{\text{body}}$$

$$\Delta S_{\text{fist}} = [(-334 \text{ J/g}) \times (18.0 \text{ g})] \div [310. \text{ K}] = -19.4 \text{ J/K} \leftarrow \text{for fist (surroundings)}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{ice}} + \Delta S_{\text{fist}}$$

$$\Delta S_{\text{total}} = +22.0 \text{ J/K} + -19.4 \text{ J/K} = +2.6 \text{ J/K} \leftarrow \text{for total (universe!)}$$

- Q5:** (i) Express the second law of thermodynamics in words.
(ii) If in a certain spontaneous process the $\Delta S_{\text{system}} = +42 \text{ J/K}$ then what can you say about $\Delta S_{\text{surroundings}}$?

- A5:** (i) For an irreversible process (a spontaneous process), the entropy of the universe is greater than zero and for a reversible process, the entropy of the universe remains the same.
(ii) $\Delta S_{\text{surroundings}}$ must decrease by less than 42 J/K.

Q6: If the pressure on a 1.00 mol sample of hydrogen gas changes from 1.00 atm to 2.00 atm at 298 K, then what is the entropy change for the sample?

A6: $\Delta S = nR \cdot \ln(P_1/P_2)$

$$\Delta S = [(1.00)(8.314)] \cdot [\ln(1.00/2.00)] = -5.76 \text{ J/K}$$

Q7: Calculate the value of the ΔS (in J/K) for a 1.00 mol sample of ethanol as it boils at 78.5°C? ($\Delta H_{\text{vaporization}} = 40.5 \text{ kJ/mol}$)

A7: $\Delta S = q_{\text{rev}}/T = \Delta H_v/T_b$

$$\Delta S = [+40500 \text{ kJ}] \div [351.5 \text{ K}] = +115 \text{ J/K}$$

Q8: Calculate the value of the ΔS for the following reaction:



A8: $\Delta S = \sum S^\circ_{f \text{ products}} - \sum S^\circ_{f \text{ reactants}}$

$$\Delta S = [S^\circ_f (\text{NH}_4\text{Cl}_{(s)})] - [S^\circ_f (\text{NH}_{3(g)}) + S^\circ_f (\text{HCl}_{(g)})]$$

$$\Delta S = [1 \text{ mol}(94.6 \text{ J/mol K})] - [1 \text{ mol}(192.5 \text{ J/mol K}) + 1 \text{ mol}(186.7 \text{ J/mol K})]$$

$$\Delta S = -284.6 \text{ J/K} \text{ this makes sense since two gases are producing a solid!}$$

Substance or Ion	ΔH_f° (kJ/mol)	S° (J/mol·K)	Substance or Ion	ΔH_f° (kJ/mol)	S° (J/mol·K)	Substance or Ion	ΔH_f° (kJ/mol)	S° (J/mol·K)
Ag(s)	0.0	42.7	CuO(s)	-155.2	43.5	MnO(s)	-384.9	60.2
Ag ¹⁺ _(aq)	+105.9	73.9	Cu ₂ O(s)	-166.7	100.8	MnO ₂ (s)	-519.7	53.1
AgBr(s)	-99.5	107.1	CuS(s)	-48.5	66.5	MnO ₄ ¹⁻ _(aq)	-518.4	190.0
AgCl(s)	-127.0	96.1	CuSO ₄ (s)	-769.9	113.4	N ₂ (g)	0.0	191.5
AgI(s)	-62.4	114.2	F ₂ (g)	0.0	203.3	Na(s)	0.0	51.0
Ag ₂ O(s)	-30.6	121.7	F ¹⁻ _(aq)	-329.1	-9.6	Na ¹⁺ _(aq)	-240.1	60.2
Ag ₂ S(s)	-31.8	145.6	Fe(s)	0.0	27.2	NaCl(s)	-411.0	72.4
Al(s)	0.0	28.3	Fe ²⁺ _(aq)	-87.9	-113.4	NaF(s)	-569.0	58.6
Al ³⁺ _(aq)	-524.7	-313.4	Fe ³⁺ _(aq)	-47.7	-293.3	NaOH(s)	-426.7	52.3
Al ₂ O ₃ (s)	-1669.8	51.0	Fe ₂ O ₃ (s)	-822.2	90.0	NH ₃ (g)	-46.2	192.5
Ba(s)	0.0	67	Fe ₃ O ₄ (s)	-1120.9	146.4	NH ₄ ¹⁺ _(aq)	-132.8	112.8
Ba ²⁺ _(aq)	-538.4	13	H ₂ (g)	0.0	130.6	NH ₄ Cl(s)	-315.4	94.6
BaCl ₂ (s)	-860.1	126	H ¹⁺ _(aq)	0.0	0.0	NH ₄ NO ₃ (s)	-365.1	151.0
BaCO ₃ (s)	-1218.8	112.1	HBr(g)	-36.2	198.5	NO(g)	+90.4	210.6
BaO(s)	-558.1	70.3	HCO ₃ ¹⁻ _(aq)	-691.1	95.0	NO ₂ (g)	+33.9	240.5
BaSO ₄ (s)	-1465.2	132.2	HCl(g)	-92.3	186.7	NO ₃ ¹⁻ _(aq)	-206.6	146.4
Br ₂ (l)	0.0	152.3	HF(g)	-268.6	173.5	Ni(s)	0.0	30.1
Br ¹⁻ _(aq)	-120.9	80.7	HI(g)	+25.9	206.3	Ni ²⁺ _(aq)	-64.0	-159.4
C(s)	0.0	5.7	HNO ₃ (l)	-173.3	155.6	NiO(s)	-244.3	38.6
CCl ₄ (l)	-139.5	214.4	H ₂ O(g)	-241.8	188.7	O ₂ (g)	0.0	205.0
CH ₄ (g)	-74.8	186.2	H ₂ O(l)	-285.8	69.9	OH ¹⁻ _(aq)	-230.0	-10.5
CHCl ₃ (l)	-131.8	202.9	H ₂ O ₂ (l)	-187.6	88.6	Pb(s)	0.0	64.9
CH ₃ OH(l)	-238.6	126.8	H ₃ PO ₄ (aq)	-1288.3	158.2	Pb ²⁺ _(aq)	+1.6	21.3
CO(g)	-100.5	197.9	H ₂ PO ₄ ¹⁻ _(aq)	-1302.5	89.1	PbBr ₂ (s)	-277.0	161.5
CO ₂ (g)	-393.5	213.6	HPO ₄ ²⁻ _(aq)	-1298.7	-36.0	PbCl ₂ (s)	-359.2	136.4
CO ₃ ²⁻ _(aq)	-676.3	-53.1	H ₂ S(g)	-20.1	205.6	PbO(s)	-217.9	69.5
C ₂ H ₂ (g)	+226.7	200.8	H ₂ SO ₄ (l)	-811.3	156.9	PbO ₂ (s)	-276.6	76.6
C ₂ H ₄ (g)	+52.3	219.5	HSO ₄ ¹⁻ _(aq)	-885.8	126.9	Pb ₃ O ₄ (s)	-734.7	211.3
C ₂ H ₆ (g)	-84.7	229.5	Hg(l)	0.0	77.4	P ₄ (s) white	0.0	41.1
C ₃ H ₈ (g)	-103.8	269.9	HgO(s)	-90.7	72.0	PCl ₃ (g)	-306.4	311.7
n-C ₄ H ₁₀ (g)	-124.7	310.0	HgS(s)	-58.2	77.8	PCl ₅ (g)	-398.9	352.7
n-C ₅ H ₁₂ (l)	-173.1	262.8	I ₂ (s)	0.0	116.7	PO ₄ ³⁻ _(aq)	-1284.1	-218
C ₂ H ₅ OH(l)	-277.6	160.7	I ¹⁻ _(aq)	-55.9	109.4	S(s)	0.0	31.9
Ca(s)	0.0	41.6	K(s)	0.0	63.6	S ²⁻ _(aq)	+41.8	22.2
Ca ²⁺ _(aq)	-543.0	-55.2	K ¹⁺ _(aq)	-251.2	102.5	SO ₂ (g)	-296.1	248.5
CaCl ₂ (s)	-795.0	113.8	KBr(s)	-392.2	96.4	SO ₃ (g)	-395.2	256.2
CaCO ₃ (s)	-1207.0	92.9	KCl(s)	-435.9	82.7	SO ₄ ²⁻ _(aq)	-907.5	17.2
CaO(s)	-635.5	39.7	KClO ₃ (s)	-391.4	143.0	Si(s)	0.0	18.7
Ca(OH) ₂ (s)	-986.6	76.1	KF(s)	-562.6	66.6	SiO ₂ (s)	-859.4	41.8
CaSO ₄ (s)	-1432.7	106.7	KI(s)	-328	106.4	Sn(s)	0.0	51.5
Cl ₂ (g)	0.0	222.9	Mg(s)	0.0	32.5	Sn ²⁺ _(aq)	-10.0	-24.7
Cl ¹⁻ _(aq)	-167.4	55.1	Mg ²⁺ _(aq)	-462.0	-118.0	SnCl ₂ (s)	-349.8	122.6
ClO ₃ ¹⁻ _(aq)	-98.3	162.3	MgCl ₂ (s)	-641.8	89.5	SnCl ₄ (l)	-545.2	258.6
ClO ₄ ¹⁻ _(aq)	-131.4	182.0	MgCO ₃ (s)	-1113	65.7	SnO(s)	-286.2	56.5
Cr(s)	0.0	23.8	MgO(s)	-601.8	26.8	SnO ₂ (s)	-580.7	52.3
CrO ₄ ²⁻ _(aq)	-863.2	38.5	Mg(OH) ₂ (s)	-924.7	63.1	Zn(s)	0.0	41.6
Cr ₂ O ₃ (s)	-1128.4	81.2	MgSO ₄ (s)	-1278.2	91.6	Zn ²⁺ _(aq)	-152.4	-106.5
Cu(s)	0.0	33.3	Mn(s)	0.0	203.3	ZnO(s)	-348.0	43.9
Cu ²⁺ _(aq)	+64.4	-98.7	Mn ²⁺ _(aq)	-462.0	-73.6	ZnS(s)	-202.9	57.5

Chapter-19

Lesson-2

III – The Molecular Interpretation of Entropy

A) Microstates:

- Molecules can undergo three types of motion: (i) translational motion, (ii) rotational motion, and (iii) vibrational motion.
- Each of these types of motion provides a molecule three different ways to distribute energy.
- A particular set of positions and energies of the individual particles for a system at any instant in time is called a **microstate**.
- The total number of possible microstates for a system is assigned the variable **W** and the entropy (S) of that system is equal to

$$S = k \cdot \ln W \quad (W \text{ is } \underline{\text{incredibly large!}})$$

where $k = 1.38 \times 10^{-23} \text{ J/K}$ and is called **Boltzmann's constant**.

- The change in entropy for a system is equal to

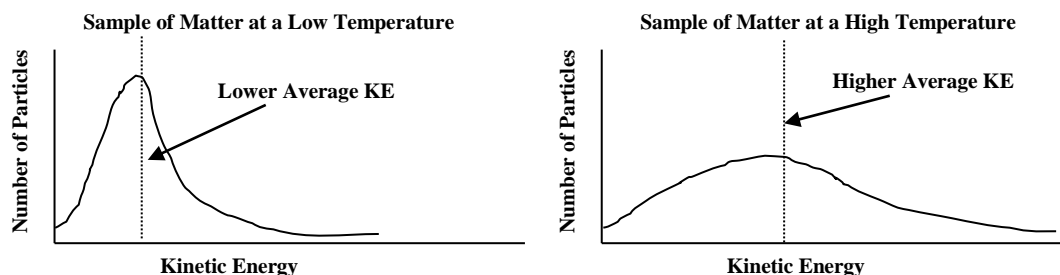
$$\Delta S = k \cdot \ln \frac{W_{\text{final}}}{W_{\text{initial}}} \quad [\text{when } W_{\text{final}} > W_{\text{initial}}, \text{ then } \Delta S \text{ is } +]$$

Thus any change in a system that leads to an increase in the number of microstates, will lead to a positive increase in entropy.

- In general, the number of microstates available to a system increases with (i) an increase in volume, (ii) an increase in temperature, or (iii) an increase in the number of independently moving molecules.
- Thus, the entropy of a system is expected to increase for any process in which (i) a solid or liquid forms a gas, (ii) a solid forms a liquid, and (iii) a chemical reaction forms more moles of gas. *Entropy often increases when a solution is formed but not always.*
- Larger atoms (Xe vs Ne) or molecules (CO₂ vs CO) have higher entropy than smaller atoms or molecules.

Q1: Explain, in terms of microstates, why an increase temperature leads to an increase in entropy.

A1: An increase in the temperature of a sample of matter leads to a broader distribution of possible kinetic energies for the molecules, thus there are more possible microstates available.



Q2: Explain, in terms of microstates, why an increase in volume leads to an increase in entropy.

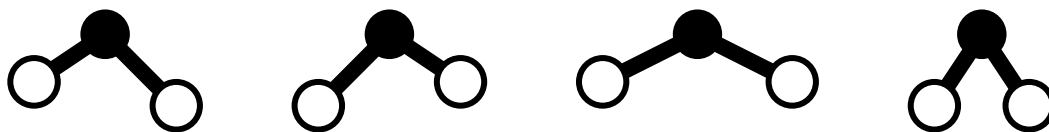
A2: An increase in the volume of a sample of matter leads to a greater number of possible positions for the molecules, thus there are more possible microstates available.

Q3: Explain, in terms of microstates, why an increase in the number of independently moving molecules in a system leads to an increase in entropy.

A3: An increase in the number of independently moving molecules leads directly to an increase in the possible number of microstates available.

Q4: Explain, in terms of microstates, why 1 mole of $\text{NO}_{2(g)}$ at STP has a greater entropy than 1 mole of $\text{NO}_{(g)}$ at STP

A4: The molecules of $\text{NO}_{2(g)}$ have a greater number of possible vibrational motions available to them, thus there are more possible microstates available.



B) Types of Work (Reviewed):

- In chemistry the two most important types of work are:
 - **PΔV work** is work done by moving (expanding) gases.

If $PΔV = (+)$, then $w = (-)$!

Thus, $+w = -PΔV$ or $-w = +PΔV$

- **electrical work** is work done by moving charged particles.

Q5: Calculate the “w” when a 22.4 L sample of gas at 273 K expands to 24.5 L as it is heated to 298 K under 1.00 atm pressure.

A5: $w = -PΔV$

$$w = -(1.00 \text{ atm})(+2.1 \text{ L})$$

$$w = -2.1 \text{ atm}\cdot\text{L} \rightarrow \boxed{-210 \text{ J of work}} \quad [\text{recall } 1 \text{ atm}\cdot\text{L} = 101.3 \text{ J}]$$

C) The First Law of Thermodynamics (Reviewed):

- The first law of thermodynamics states that the energy of a system plus the energy of its surroundings remains constant.

$$\text{Thus ... } \Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$$

This is the **law of conservation of energy**.

- Recall that the first law of thermodynamics also has the form

$$\Delta E_{\text{system}} = q + w$$

where $\Delta E_{\text{system}} = [\Sigma \text{ KE} + \Sigma \text{ PE}]$, q = heat flow, w = work done

- Here heat (q) is distinguished from all other forms of energy, referred collectively as work (w).
- When heat is flowing into the system from the surroundings then q is (+) and when heat is flowing out of the system to the surroundings then q is (−).
- When work is done on the system by the surroundings the w is (+) and when work is done by the system on the surroundings then w is (−).

Q6: Calculate the ΔE_{system} when the system absorbs 519 J of heat as it does 210 J of work on the surroundings.

A6: $\Delta E_{\text{system}} = q + w$

$$\Delta E_{\text{system}} = (+ 519 \text{ J}) + (-210 \text{ J})$$

$$\Delta E_{\text{system}} = \boxed{+309 \text{ J}}$$

D) The Second Law of Thermodynamics (Reviewed):

- Although all other forms of energy (work) can be converted into heat, there is a restriction in converting heat into work! (OOO!)
- There are several ways to state the second law of thermodynamics:
 - The entropy of the universe is constantly increasing.

$$\Delta S_{\text{universe}} > 0$$

- A change will occur spontaneously only when there is an increase in entropy of the universe.
 - Heat cannot be completely converted to work in an engine operating in cycles at constant temperature. **THUS**, in all engines, the energy used is always greater than the work done.
- A consequence of the second law of thermodynamics is that no engine can be 100% efficient. In fact, the maximum efficiency of an *ideal* (Carnot) heat engine is...

$$\text{max. efficiency} = \frac{T_2 - T_1}{T_2} = \frac{w}{q}$$

where **w** is the work done, **q** is the heat absorbed at the high temp., **T₂** is the high kelvin temperature and **T₁** is the low kelvin temp.

Q7: If the heat delivered to the firing chamber is 2.86×10^7 kJ and if the amount of useful mechanical energy produced is 1.20×10^7 kJ, then calculate the actual efficiency of the engine.

A7: actual efficiency = $(1.20 \times 10^7) / (2.86 \times 10^7) = 0.42$ or **42%**

E) The Third Law of Thermodynamics

- As a system is cooled, the number of microstates decreases.
- As a pure substance perfectly solidifies and is then cooled to 0 Kelvin, the number of microstates decreases to 1 microstate.
- The **third law of thermodynamics** states:
(*Chemists would say...*) that the entropy of a **perfect** pure crystalline substance is zero at absolute zero! $S = k \cdot \ln W$
(*Physicists would say...*) that a heat engine achieves 100% efficiency if the low temperature reservoir is lowered to absolute zero. $\% \text{Efficiency} = [(T_{\text{Hi}} - T_{\text{Lo}})/T_{\text{Hi}}] \times 100$

Q8: For each of the following pairs, predict which substance has the higher molar entropy at a given temperature and explain why.

- (i) 1 mole $\text{NO}_{(\text{g})}$ in 5 L or 1 mole $\text{NO}_{(\text{g})}$ in 1 L
- (ii) 1 mole $\text{Ne}_{(\text{g})}$ at 2 atm or 1 mole $\text{Ne}_{(\text{g})}$ at 1 atm
- (iii) 1 mole $\text{CO}_{(\text{g})}$ at STP or 1 mol $\text{CO}_{2(\text{g})}$ at STP
- (iv) 1 mole $\text{I}_{2(\text{g})}$ or 1 mol $\text{I}_{2(\text{s})}$

A8: (i) $\text{NO}_{(\text{g})}$ in 5 L because in a larger volume the total possible set of microstates is larger.

(ii) $\text{Ne}_{(\text{g})}$ at 1 atm because at lower pressure there is a larger volume thus the total possible set of microstates is larger.

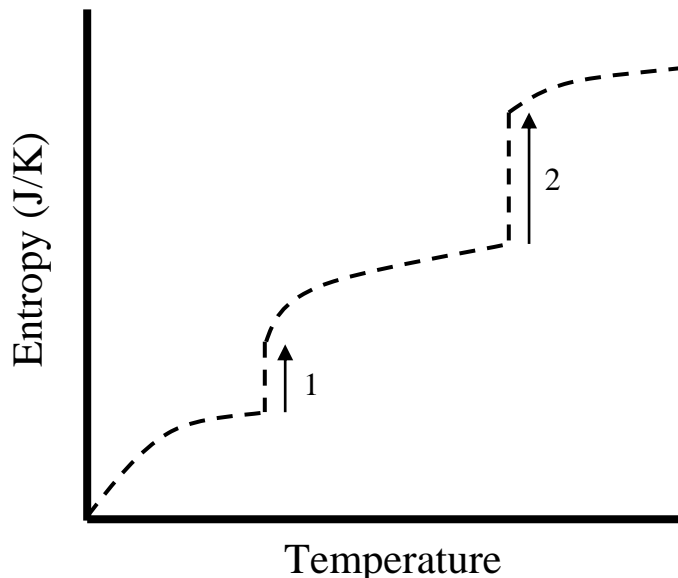
(iii) $\text{CO}_{2(\text{g})}$ because its molecules have a greater number of possible vibrational motions available compared to $\text{CO}_{(\text{g})}$ thus $\text{CO}_{2(\text{g})}$ has a greater total possible set of microstates.

(iv) $\text{I}_{2(\text{g})}$ because a gas has a greater total possible set of microstates than a solid.

Q9: Predict whether the entropy increases (+ ΔS) or decreases (- ΔS) for the following processes: (i) $\text{HCl}_{(\text{g})} + \text{NH}_{3(\text{g})} \rightarrow \text{NH}_4\text{Cl}_{(\text{s})}$
(ii) $\text{KI}_{(\text{s})} \rightarrow \text{K}^{1+}_{(\text{aq})} + \text{I}^{1-}_{(\text{aq})}$ (iii) $2 \text{SO}_{3(\text{g})} \rightarrow 2 \text{SO}_{2(\text{g})} + \text{O}_{2(\text{g})}$

A9: (i) decreases (- ΔS) (ii) increases (+ ΔS) (iii) increases (+ ΔS)

Q10: The diagram below shows the variation in entropy with temperature for a substance that is in the gas phase at the highest temperature shown. (i) What processes correspond to each of the entropy increases along the vertical lines labeled 1 and 2? (ii) Why is the entropy change for 2 larger than that for 1?



A10: (i) The vertical entropy increases represent phase changes (#1 = melting and #2 = vaporization).
(ii) The ΔS for vaporization is always larger than the ΔS for melting because of the large volume increase of the system.

Q11: Even in the solid phase the particles that compose the crystal are vibrating around their position in the lattice and thus there are still multiple sets of possible microstates. However, at absolute zero all motion stops. (i) At absolute zero, how many possible microstates are available in a perfect solid crystal? (ii) Using Boltzmann's equation ($S = k \cdot \ln W$) explain why at absolute zero the entropy of a perfect crystal is zero.

A11: (i) Since the particles are not moving, then the total number of possible microstates is equal to one ($W = 1$).
(ii) If at absolute zero there is only one microstate ($W = 1$), then in Boltzmann's equation ($S = k \cdot \ln W$), entropy is equal to zero ($S = 0$).

Chapter-19

Lesson-3

IV – Entropy Changes in Chemical reactions

A) Standard Molar Entropies of Elements & Compounds:

- All substances, elements and compounds, have some disorder above absolute zero (0 K) thus all entropy values are positive.
- Entropy values for pure substances, elements and compounds, are absolute values NOT relative values.
- Molar entropy values for pure substances generally increase with: (1) an increase in the number of atoms in the formula. (2) an increase in the number of ways in which the molecules of the substance can bend or spin. (3) or all else being equal, with an increase in molar mass of the substance.
- Standard molar entropy values (S°) are usually given in units of *joules per kelvin* (J/K) at 25°C and 1 atm.

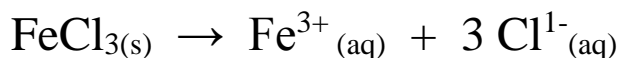
B) Standard Molar Entropies of Aqueous Ions:

- Entropy values for aqueous ions are relative values based on the arbitrary decision to assign the value of zero for the standard molar entropy of the aqueous hydrogen ion ($S^\circ \text{H}^+_{(\text{aq})} = 0$).
- Standard molar entropy values of aqueous ions can be (+) or (–).
- Standard molar entropy values of aqueous ions (S°) are usually given in units of *joules per kelvin* (J/K) at 25°C and 1 atm.

C) The Standard Entropy Change (ΔS°) for Reactions

- For a reaction; $\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$

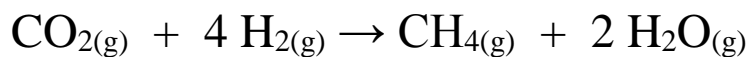
Q1: Using appendix C, calculate the ΔS° for



A1: $\Delta S = [(293.3) + 3(56.5)] - [(142.3)]$

$$\Delta S = [462.8] - [142.3] = \boxed{+320.5 \text{ J/mol}\cdot\text{K}} \text{ (an increase in entropy)}$$

Q2: Using appendix C, calculate the ΔS° for



A2: $\Delta S = [(186.3) + 2(188.83)] - [(213.6) + 4(130.58)]$

$$\Delta S = [564.0] - [738.9] = [-174.9 \text{ J/mol}\cdot\text{K}] \text{ (a decrease in entropy)}$$

V – Gibb's Free Energy

- Neither the enthalpy change (ΔH) nor the entropy change (ΔS) alone determines the spontaneity of a reaction.
- There is a third thermodynamic quantity that determines the spontaneity of a reaction - the **free energy change** (ΔG).
- **Free energy** is a measure of “*the maximum amount of useful work*” that can be performed by a system.
- If the ΔG for a reaction (at constant temp. and pressure) is...
 - **negative** then the reaction is spontaneous.
 - **positive** then the reaction is nonspontaneous (*the reverse is*).
 - **zero** then the reaction is in a state of equilibrium with the reverse reaction.

A) The Gibbs-Helmholtz Equation:

- **Free energy** (G) is a function of enthalpy (H) and entropy (S).
- The relationship between enthalpy (H) and entropy (S) is called the **Gibbs-Helmholtz equation**.

$$G = H - TS \quad (\text{where } T \text{ is Kelvin temperature})$$

- **Free energy change** (ΔG) is a measure of the maximum amount of useful work that can be obtained at constant temperature and pressure.

$$\Delta G = \Delta H - T\Delta S$$

- When all the components of a system are in their standard states (1 atm for gases and 1 M for solutions), then...

$$\Delta G^\circ_{\text{sys}} = \Delta H^\circ_{\text{sys}} - T\Delta S^\circ_{\text{sys}}$$

and in this way the free energy changes of different reactions can be compared to each other.

- ☞ Unlike ΔH° or ΔS° , ΔG° is very **strongly** temperature dependent.

B) Calculation of ΔG° : $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

- If $\Delta H^\circ = (+)$ and $\Delta S^\circ = (-)$, then $\Delta G^\circ = (+)$ and the reaction is nonspontaneous at all temperatures.
- If $\Delta H^\circ = (-)$ and $\Delta S^\circ = (+)$, then $\Delta G^\circ = (-)$ and the reaction is spontaneous at all temperatures.
- If $\Delta H^\circ = (+)$ and $\Delta S^\circ = (+)$, then $\Delta G^\circ = (+)$ at low temperatures and the reaction is nonspontaneous **but** at high temperatures, $\Delta G^\circ = (-)$, and the reaction becomes spontaneous.

Example: the melting of ice.

- If $\Delta H^\circ = (-)$ and $\Delta S^\circ = (-)$, then $\Delta G^\circ = (+)$ at high temperatures and the reaction is nonspontaneous **but** at low temperatures, $\Delta G^\circ = (-)$, and the reaction becomes spontaneous.

Example: the freezing of water.

Q3: What is the ΔG° for the reduction of iron (III) oxide with hydrogen gas at 25.0°C?

A3: the reaction is ... $\text{Fe}_2\text{O}_{3(s)} + 3 \text{H}_{2(g)} \rightarrow 2 \text{Fe}_{(s)} + 3 \text{H}_2\text{O}_{(g)}$

$$\Delta H^\circ = [2(0) + 3(-241.8)] - [(-822.2) + 3(0)] = \underline{+ 96.8 \text{ kJ}}$$

$$\Delta S^\circ = [2(27.2) + 3(188.8)] - [(90.0) + 3(130.6)] = \underline{+ 139.0 \text{ J/K}}$$

$$\Delta G^\circ = [+ 96.8] - 298.0[+ 0.1390] = \boxed{+ 55.4 \text{ kJ}} \text{ (nonspontaneous!)}$$

Q4: What is the ΔG° for the reduction of iron (III) oxide with hydrogen gas at 500.0°C?

$$\textbf{A4: } \Delta G^\circ = [+ 96.8] - 773.0[+ 0.1390] = \boxed{- 10.6 \text{ kJ}} \text{ (spontaneous!)}$$

Q5: At what minimum temperature is the reduction of iron (III) oxide with hydrogen gas spontaneous?

A5: At this temperature, ΔG° will equal zero! Thus...

$$\Delta G^\circ = 0 = [+ 96.8] - T[+ 0.1390] \rightarrow T = \boxed{696 \text{ K or } 423^\circ\text{C}}$$

C) Temperatures at which Reactions become Spontaneous:

- A nonspontaneous reaction, $\Delta G = (+)$, just becomes spontaneous when $\Delta G = (0)$. Thus...

$$T = \Delta H / \Delta S \rightarrow \text{[the moment a nonspontaneous reaction becomes spontaneous]}$$

This is the temperature at which reactions become spontaneous!

- In the case of **boiling**, this equation becomes...

$$T_b = \Delta H_v / \Delta S_v$$

Q6: Calculate the normal boiling point of mercury if the standard heat of vaporization (ΔH_v°) is +60.8 kJ/mol and the standard entropy of vaporization (ΔS_v°) is +0.0975 kJ/mol•K.

A6: $T_b = \Delta H_v^\circ / \Delta S_v^\circ = +60.8 / +0.0975 =$ **624 K or 351°C**

Q7: If the normal boiling point of liquid bromine is 332 K and the standard heat of vaporization is +30.7 kJ/mol, then calculate the standard entropy of vaporization.

A7: $T_b = \Delta H_v^\circ / \Delta S_v^\circ$

$$332 = +30.7 / \Delta S_v^\circ$$

$$\Delta S_v^\circ =$$
 +0.0925 kJ/mol•K

If you can experimentally determine a liquid's T_b , you can estimate the liquid's H_v

☞ Notice that in both problems the $\Delta S_v^\circ \approx +0.09$ kJ/mol•K!

This approximation is known as **Trouton's rule**: when 1 mol of any substance is changed from liquid to vapor at its normal boiling point, the entropy will increase about + 0.09 kJ/mol•K!

Q8: Based on the outcome in question #7, calculate the standard molar entropy of bromine vapor in J/K.

A8: $\Delta S_v^\circ = S^\circ_{(g)} - S^\circ_{(\ell)}$

$$(+92.5 \text{ J/K}) = (S^\circ_{(g)}) - (+152.3 \text{ J/K})$$

$$S^\circ_{(g)} =$$
 244.8 J/K

Q9: What is the ΔG° for the reaction of solid magnesium metal in liquid water at 25.0°C?

A9: the reaction is ... $\text{Mg}_{(s)} + 2 \text{H}_2\text{O}_{(l)} \rightarrow \text{Mg}^{2+}_{(aq)} + 2 \text{OH}^{-}_{(aq)} + \text{H}_{2(g)}$

$$\Delta H^\circ = [(-462.0) + 2(-230.0) + 1(0)] - [(0) + 2(-285.8)]$$

$$\Delta H^\circ = \underline{\underline{-350.4 \text{ kJ}}}$$

$$\Delta S^\circ = [(-118.0) + 2(-10.5) + 1(130.6)] - [(32.5) + 2(69.9)]$$

$$\Delta S^\circ = \underline{\underline{-180.7 \text{ J/K}}} \text{ (very weird!)}$$

$$\Delta G^\circ = [-350.4] - 298.0[-0.1807] = \boxed{-296.6 \text{ kJ}} \text{ (spontaneous!)}$$

Q10: What is the ΔG° for the reaction of solid magnesium metal in liquid water at 100.0°C?

$$\underline{\underline{\text{A10}}}: \Delta G^\circ = [-350.4] - 373.0[-0.1807] = \boxed{-283.0 \text{ kJ}} \text{ (spontaneous!)}$$

Q11: The heat of vaporization of argon is +6.3 kJ/mol.

- (i) Estimate the boiling point of argon using Trouton's rule.
- (ii) If the boiling point of argon is -186 °C, then calculate the ΔS°_v for argon

A11: (i) $T_b = \Delta H^\circ_v / \Delta S^\circ_v$

$$T_b \approx (+6.3 \text{ kJ}) / (+0.09 \text{ kJ/K})$$

$$T_b \approx \boxed{70 \text{ K or } -203^\circ\text{C}}$$

(ii) $T_b = \Delta H^\circ_v / \Delta S^\circ_v$

$$90. \text{ K} \approx (+6.3 \text{ kJ}) / (\Delta S_v)$$

$$\Delta S_v = \boxed{+0.070 \text{ kJ/K}}$$

Substance or Ion	ΔH_f° (kJ/mol)	S° (J/mol·K)	Substance or Ion	ΔH_f° (kJ/mol)	S° (J/mol·K)	Substance or Ion	ΔH_f° (kJ/mol)	S° (J/mol·K)
Ag(s)	0.0	42.7	CuO(s)	-155.2	43.5	MnO(s)	-384.9	60.2
Ag ¹⁺ _(aq)	+105.9	73.9	Cu ₂ O(s)	-166.7	100.8	MnO ₂ (s)	-519.7	53.1
AgBr(s)	-99.5	107.1	CuS(s)	-48.5	66.5	MnO ₄ ¹⁻ _(aq)	-518.4	190.0
AgCl(s)	-127.0	96.1	CuSO ₄ (s)	-769.9	113.4	N ₂ (g)	0.0	191.5
AgI(s)	-62.4	114.2	F ₂ (g)	0.0	203.3	Na(s)	0.0	51.0
Ag ₂ O(s)	-30.6	121.7	F ¹⁻ _(aq)	-329.1	-9.6	Na ¹⁺ _(aq)	-240.1	60.2
Ag ₂ S(s)	-31.8	145.6	Fe(s)	0.0	27.2	NaCl(s)	-411.0	72.4
Al(s)	0.0	28.3	Fe ²⁺ _(aq)	-87.9	-113.4	NaF(s)	-569.0	58.6
Al ³⁺ _(aq)	-524.7	-313.4	Fe ³⁺ _(aq)	-47.7	-293.3	NaOH(s)	-426.7	52.3
Al ₂ O ₃ (s)	-1669.8	51.0	Fe ₂ O ₃ (s)	-822.2	90.0	NH ₃ (g)	-46.2	192.5
Ba(s)	0.0	67	Fe ₃ O ₄ (s)	-1120.9	146.4	NH ₄ ¹⁺ _(aq)	-132.8	112.8
Ba ²⁺ _(aq)	-538.4	13	H ₂ (g)	0.0	130.6	NH ₄ Cl(s)	-315.4	94.6
BaCl ₂ (s)	-860.1	126	H ¹⁺ _(aq)	0.0	0.0	NH ₄ NO ₃ (s)	-365.1	151.0
BaCO ₃ (s)	-1218.8	112.1	HBr(g)	-36.2	198.5	NO(g)	+90.4	210.6
BaO(s)	-558.1	70.3	HCO ₃ ¹⁻ _(aq)	-691.1	95.0	NO ₂ (g)	+33.9	240.5
BaSO ₄ (s)	-1465.2	132.2	HCl(g)	-92.3	186.7	NO ₃ ¹⁻ _(aq)	-206.6	146.4
Br ₂ (l)	0.0	152.3	HF(g)	-268.6	173.5	Ni(s)	0.0	30.1
Br ¹⁻ _(aq)	-120.9	80.7	HI(g)	+25.9	206.3	Ni ²⁺ _(aq)	-64.0	-159.4
C(s)	0.0	5.7	HNO ₃ (l)	-173.3	155.6	NiO(s)	-244.3	38.6
CCl ₄ (l)	-139.5	214.4	H ₂ O(g)	-241.8	188.7	O ₂ (g)	0.0	205.0
CH ₄ (g)	-74.8	186.2	H ₂ O(l)	-285.8	69.9	OH ¹⁻ _(aq)	-230.0	-10.5
CHCl ₃ (l)	-131.8	202.9	H ₂ O ₂ (l)	-187.6	88.6	Pb(s)	0.0	64.9
CH ₃ OH(l)	-238.6	126.8	H ₃ PO ₄ (aq)	-1288.3	158.2	Pb ²⁺ _(aq)	+1.6	21.3
CO(g)	-100.5	197.9	H ₂ PO ₄ ¹⁻ _(aq)	-1302.5	89.1	PbBr ₂ (s)	-277.0	161.5
CO ₂ (g)	-393.5	213.6	HPO ₄ ²⁻ _(aq)	-1298.7	-36.0	PbCl ₂ (s)	-359.2	136.4
CO ₃ ²⁻ _(aq)	-676.3	-53.1	H ₂ S(g)	-20.1	205.6	PbO(s)	-217.9	69.5
C ₂ H ₂ (g)	+226.7	200.8	H ₂ SO ₄ (l)	-811.3	156.9	PbO ₂ (s)	-276.6	76.6
C ₂ H ₄ (g)	+52.3	219.5	HSO ₄ ¹⁻ _(aq)	-885.8	126.9	Pb ₃ O ₄ (s)	-734.7	211.3
C ₂ H ₆ (g)	-84.7	229.5	Hg(l)	0.0	77.4	P ₄ (s) white	0.0	41.1
C ₃ H ₈ (g)	-103.8	269.9	HgO(s)	-90.7	72.0	PCl ₃ (g)	-306.4	311.7
n-C ₄ H ₁₀ (g)	-124.7	310.0	HgS(s)	-58.2	77.8	PCl ₅ (g)	-398.9	352.7
n-C ₅ H ₁₂ (l)	-173.1	262.8	I ₂ (s)	0.0	116.7	PO ₄ ³⁻ _(aq)	-1284.1	-218
C ₂ H ₅ OH(l)	-277.6	160.7	I ¹⁻ _(aq)	-55.9	109.4	S(s)	0.0	31.9
Ca(s)	0.0	41.6	K(s)	0.0	63.6	S ²⁻ _(aq)	+41.8	22.2
Ca ²⁺ _(aq)	-543.0	-55.2	K ¹⁺ _(aq)	-251.2	102.5	SO ₂ (g)	-296.1	248.5
CaCl ₂ (s)	-795.0	113.8	KBr(s)	-392.2	96.4	SO ₃ (g)	-395.2	256.2
CaCO ₃ (s)	-1207.0	92.9	KCl(s)	-435.9	82.7	SO ₄ ²⁻ _(aq)	-907.5	17.2
CaO(s)	-635.5	39.7	KClO ₃ (s)	-391.4	143.0	Si(s)	0.0	18.7
Ca(OH) ₂ (s)	-986.6	76.1	KF(s)	-562.6	66.6	SiO ₂ (s)	-859.4	41.8
CaSO ₄ (s)	-1432.7	106.7	KI(s)	-328	106.4	Sn(s)	0.0	51.5
Cl ₂ (g)	0.0	222.9	Mg(s)	0.0	32.5	Sn ²⁺ _(aq)	-10.0	-24.7
Cl ¹⁻ _(aq)	-167.4	55.1	Mg ²⁺ _(aq)	-462.0	-118.0	SnCl ₂ (s)	-349.8	122.6
ClO ₃ ¹⁻ _(aq)	-98.3	162.3	MgCl ₂ (s)	-641.8	89.5	SnCl ₄ (l)	-545.2	258.6
ClO ₄ ¹⁻ _(aq)	-131.4	182.0	MgCO ₃ (s)	-1113	65.7	SnO(s)	-286.2	56.5
Cr(s)	0.0	23.8	MgO(s)	-601.8	26.8	SnO ₂ (s)	-580.7	52.3
CrO ₄ ²⁻ _(aq)	-863.2	38.5	Mg(OH) ₂ (s)	-924.7	63.1	Zn(s)	0.0	41.6
Cr ₂ O ₃ (s)	-1128.4	81.2	MgSO ₄ (s)	-1278.2	91.6	Zn ²⁺ _(aq)	-152.4	-106.5
Cu(s)	0.0	33.3	Mn(s)	0.0	203.3	ZnO(s)	-348.0	43.9
Cu ²⁺ _(aq)	+64.4	-98.7	Mn ²⁺ _(aq)	-462.0	-73.6	ZnS(s)	-202.9	57.5

Chapter-19

Lesson-4

VI – Free Energy and Equilibrium

- The ΔG for a system at *nonstandard conditions* is equal to

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where both ΔG and ΔG° is in J/mol, $R = 8.314 \text{ J/mol}\cdot\text{K}$, T is in Kelvin, and Q is the value of the reaction quotient.

Q1: Calculate the ΔG° for the reaction $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$ at **25°C**. Use appendix C.

A1: $\Delta G^\circ = \sum \Delta G^\circ_{\text{f of products}} - \sum \Delta G^\circ_{\text{f of reactants}}$

$$\Delta G^\circ = [2(-16.7)] - [(0) + 3(0)]$$

$$\Delta G^\circ = \boxed{-33.4 \text{ kJ}}$$

Q2: Calculate the ΔG° for the reaction $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$ at **227°C (not at 25.0°C)**. Use appendix C.

A2: $\Delta H^\circ = \sum \Delta H^\circ_{\text{f of products}} - \sum \Delta H^\circ_{\text{f of reactants}}$

$$\Delta H^\circ = [2(-46.2)] - [(0) + 3(0)]$$

$$\Delta H^\circ = \underline{\underline{-92.4 \text{ kJ}}}$$

$$\Delta S^\circ = \sum S^\circ_{\text{f of products}} - \sum S^\circ_{\text{f of reactants}}$$

$$\Delta S^\circ = [2(192.5)] - [(191.5) + 3(130.6)]$$

$$\Delta S^\circ = \underline{\underline{-198.3 \text{ J/K}}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = [(-92.4)] - [(500)(-0.1983)]$$

$$\Delta G^\circ = \boxed{+6.8 \text{ kJ}} \text{ at } 227^\circ\text{C, the reaction is nonspontaneous}$$

Q3: Calculate the ΔG for the reaction $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$ at **25°C** that consists of a mixture of 1.0 atm N_2 , 3.0 atm H_2 , and 1 atm NH_3 .

A3: $Q = \frac{(1.0)^2}{(1.0)(3.0)^3}$

$$Q = 0.037$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = (-33400) + (8.314)(298)[\ln(0.037)]$$

$$\Delta G = \boxed{-41600 \text{ J or } -41.6 \text{ kJ}}$$

Q4: Calculate the ΔG for the reaction $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$ at **227°C** that consists of a mixture of 1.0 atm N_2 , 3.0 atm H_2 , and 1 atm NH_3 .

A4: $\Delta G = \Delta G^\circ + RT \ln Q$

$$\Delta G = (+6800) + (8.31)(500)[\ln(0.037)]$$

$$\Delta G = \boxed{-6900 \text{ J or } -6.9 \text{ kJ}}$$

*The reaction is spontaneous at these nonstandard conditions.
Thus the “point of equilibrium” is some “place to the right”!*

- The equilibrium constant (K) determines the **extent** of a reaction.
- Free energy (ΔG) determines the spontaneity of a reaction, which in a sense determines the **extent** of a reaction.
- As you might expect, the equilibrium constant (K) and free energy (ΔG) are intimately related. *For systems at equilibrium, $\Delta G = 0$* , and thus the equation

$$\Delta G = \Delta G^\circ + RT \ln Q$$

becomes

$$\Delta G^\circ = -RT \ln K$$

where ΔG° is in J/mol, $R = 8.314 \text{ J/mol}\cdot\text{K}$, T is in Kelvin, and K is the value of the equilibrium constant.

- The more negative the value of ΔG° , the larger the value of the equilibrium constant.

ΔG° kJ/mol	K at 298 K
+100	3.0×10^{-18}
+10	1.8×10^{-2}
0	1
-10	5.6×10^1
-100	3.3×10^{17}

Q5: Calculate the value of the equilibrium constant for the system
 $\text{N}_{2(\text{g})} + 3 \text{H}_{2(\text{g})} \rightleftharpoons 2 \text{NH}_{3(\text{g})}$ at **25°C**. (*See question 1*)

A5: $\Delta G^\circ = -RT \ln K$

$$-33400 = -(8.31)(298)[\ln(K)]$$

$$K = \boxed{7.20 \times 10^5}$$

Q6: Calculate the value of the equilibrium constant for the system
 $\text{N}_{2(\text{g})} + 3 \text{H}_{2(\text{g})} \rightleftharpoons 2 \text{NH}_{3(\text{g})}$ at **227°C**. (*See question 2*)

A6: $\Delta G^\circ = -RT \ln K$

$$+6800 = -(8.31)(500)[\ln(K)]$$

$$K = \boxed{0.195}$$

Q7: Calculate the K for the reaction $\text{CaCO}_{3(\text{s})} \rightleftharpoons \text{CaO}_{(\text{s})} + \text{CO}_{2(\text{g})}$ if the ΔG° for the reaction is +54.0 kJ at 500°C.

A7: $\Delta G^\circ = -RT \ln K$

$$+54000 = -(8.31)(773)(\ln K)$$

$$K = \boxed{2.23 \times 10^{-4}}$$

CaO is called quicklime or just lime. 22 million tons is produced annually in the USA. When mixed with H₂O it becomes Ca(OH)₂, an important commercial base. When mixed with sand and water, it becomes mortar.

Student Activity-5: The Thermodynamic Favorability of Reactions

Q8: In the previous problem, the decomposition of $\text{CaCO}_{3(s)}$ was not thermodynamically favored at 500°C . Predict the minimum temperature needed to spontaneously convert $\text{CaCO}_{3(s)}$ to $\text{CaO}_{(s)}$.



Chemical Name	Common Name	ΔH° kJ/mol	ΔS° J/mol·K
$\text{CaCO}_{3(s)}$	Limestone	-1207.1	92.88
$\text{CaO}_{(s)}$	Quicklime	-635.5	39.75
$\text{CO}_{2(g)}$	—	-393.5	213.6

A8: $\Delta H^\circ = \sum \Delta H^\circ_{\text{f of products}} - \sum \Delta H^\circ_{\text{f of reactants}}$

$$\Delta H^\circ = [1(-635.5) + 1(-393.5)] - [1(-1207.1)]$$

$$\Delta H^\circ = \underline{+178.1 \text{ kJ}}$$

$$\Delta S^\circ = \sum S^\circ_{\text{f of products}} - \sum S^\circ_{\text{f of reactants}}$$

$$\Delta S^\circ = [1(39.75) + 1(213.6)] - [1(92.88)]$$

$$\Delta S^\circ = \underline{+160.5 \text{ J/K}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$0 = [(+178.1)] - [(X)(+0.1605)]$$

$$T = \boxed{1110. \text{ K or } 837^\circ\text{C}}$$

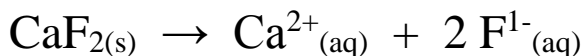
Q9: The K_{sp} of $\text{CaF}_{2(s)}$ at 25°C is 3.0×10^{-11} . (i) Calculate the ΔG° for the dissolving of CaF_2 in water at 25°C using the K_{sp} value.

A9: $\Delta G^\circ = -RT \ln K$

$$\Delta G^\circ = -(8.31)(298) \ln 3.0 \times 10^{-11}$$

$$\Delta G^\circ = \boxed{+6.00 \times 10^4 \text{ J/mol} \rightarrow +60.0 \text{ kJ/mol}}$$

Q10: Using the enthalpy and entropy data below, (i) calculate the ΔG° for the dissolving of $\text{CaF}_{2(s)}$ in water at 25°C . (ii) Explain why dissolving $\text{CaF}_{2(s)}$ in water results in a decrease in entropy!



	$\Delta H^\circ \text{ kJ/mol}$	$\Delta S^\circ \text{ J/mol}\cdot\text{K}$
$\text{CaF}_{2(s)}$	-1215.0	68.9
$\text{Ca}^{2+}_{(aq)}$	-543.0	-55.2
$\text{F}^{-}_{(aq)}$	-329.1	-13.8

A10: (i) $\Delta H^\circ = \sum \Delta H^\circ_{\text{f of products}} - \sum \Delta H^\circ_{\text{f of reactants}}$

$$\Delta H^\circ = [1(-543.0) + 2(-329.1)] - [1(-1215.0)]$$

$$\Delta H^\circ = \underline{\underline{+13.8 \text{ kJ/mol}}}$$

$$\Delta S^\circ = \sum S^\circ_{\text{f of products}} - \sum S^\circ_{\text{f of reactants}}$$

$$\Delta S^\circ = [1(-55.2) + 2(-13.8)] - [1(68.9)]$$

$$\Delta S^\circ = \underline{\underline{-151.7 \text{ J/mol}\cdot\text{K}}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = [(+13.8)] - [(298)(-0.1517)]$$

$$\Delta G^\circ = \boxed{+55.5 \text{ kJ/mol}}$$

(ii) The hydration of ions often has an “order producing effect” on the water molecules especially if the ions are small or have a high charge. If this “order producing effect” on the water molecules by the dissolved ions is greater than the “disorder producing effect” caused by the separation of the ions from each other, then the overall entropy change of the dissolution process will be negative.